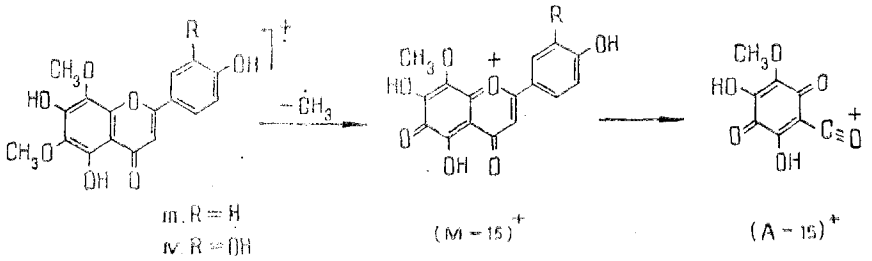

III. R = H
IV. R = OH

A mass-spectrometric study of compounds (III) and (IV) confirmed their structures. The main process of fragmentation of flavones with 6- or 8-OR groups (R = CH_3) was a pathway leading to the loss of the radical and the formation of the ion (M − R), which is not infrequently the main peak of the spectrum. The subsequent loss of CO from this ion produced the fragment (M − R − CO). This process was completed by the quinoid ions (A − R) and (A − R − CO) [4] formed from peak A in the decomposition of the ion (M − R).

It is just these ions that were present in the mass spectra of (III) and (IV), the ions (A − 15) with m/z 197 and (A − 43) with m/z 169 having identical masses in each case, since this part of the spectrum is common to the two compounds.

It must be mentioned that flavonoids with completely substituted rings A are comparatively rare in nature. Thus, 3',4',5,7-tetrahydroxy-6,8-dimethoxyflavone (IV) has previously been isolated only from the gardenia (family Rubiaceae) [5], and 4',5,7-trihydroxy-6,8-dimethoxyflavone (III) from only three plants [6].

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FLAVONOIDS OF THE RHIZOMES OF *Rhodiola rosea*. III.

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Derivatives of tricin and herbacetin have been isolated previously from the rhizomes of *Rhodiola rosea* L. (roseroot stonecrop), family Crassulaceae [1, 2]. Continuing an investigation of the rhizomes of this plant, we have isolated another four flavonoid compounds (I-IV) and a gallic acid derivative (V).

Compound (I) forms yellow crystals from aqueous acetone with the composition $C_{16}H_{12}O_7$, M^+ 316, mp 262-264°C (decomp.). The PMR spectrum of this compound (in deuteroacetone) contained the signals of the protons of a herbacetin skeleton [two doublets J = 9 Hz at 8.23 ppm (H-2',6') and 7.06 ppm (H-3',5'), and a singlet of H-6 at 6.34 ppm] and the singlet signal of one methoxy group at 3.99 ppm.

The mass-spectrometric fragmentation of (I) with the formation of the ions $(M - 15)^+$, 301 (100%), A − 15, with m/z 167, and A − 43 with m/z 139, indicated the presence of a methoxy group in ring A [3]. The small bathochromic shifts ($\Delta\lambda$ = 9 mm) of the short-wave maximum in the UV spectrum in the presence of sodium acetate indicated the presence of free 7-OH group. The long-wave maximum in the UV spectrum in MeOH at 374 nm permitted this com-

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pound to be assigned to the flavones with a free 3-OH group, and the large bathochromic shift ($\Delta\lambda$ = 64 nm) of band I in the presence of $AlCl_3$ + HCl showed, in addition, a free 5-OH group. The UV and mass spectra showed the presence of free 4'-OH group (ion B with m/z 121). The fact given and also the negative reaction of compound (I) with p-benzoquinone enable it to be characterized as 8-methylherbacetin [4].

Compound (II) formed bright yellow crystals with the composition $C_{22}H_{20}O_{11}$, mp 225-227°C, $[\alpha]_D^{20}$ +69.2° (c 0.8; methanol) which split on acid hydrolysis into herbacetin and arabinose, the attachment of which to the 8-OH group was shown by analogy with 8-methylherbacetin.

Furthermore, according to the PMR spectrum (deuteropyridine), the carbohydrate fragment contained an acetyl group (singlet at 1.90 ppm) which was assigned to the third hydroxyl of the sugar, since at 5.58 ppm the signal of the C-3" proton of the arabinose appeared in the form of a doublet of doublets with J = 3 and 8 Hz. Consequently, compound (II) was identical with the acetylrhodalgin isolated previously from *Rhodiola algida* [5].

Compound (III) formed yellow crystals with the composition $C_{21}H_{20}O_{10}$ with mp 238-241°C (aqueous ethanol), $[\alpha]_D^{20}$ −140° (c 0.8; methanol), and was identified as kaempferol 7-O-α-L-rhamnopyranoside on the basis of its UV and PMR spectra. The acid hydrolysis of (III) gave rhamnose and kaempferol (compound (IV), M^+ 286), which was also isolated from the plant in the free form.

Compound (V) formed white crystals with a greyish tinge having the composition $C_8H_8O_5$, M^+ 184, mp 188-191°C (water). Its PMR spectrum (deuteroacetone) contained the singlet signal of aromatic protons at 7.20 ppm and the singlet signal of one OCH_3 at 3.84 ppm, which, in combination with the IR spectrum (ester band at 1680 cm^{-1}) and mass spectra (ions with m/z 170 and 153 (100)), enabled compound (V) to be identified as methyl gallate.

The identification of compounds (II-V) was also carried out by direct comparison with authentic samples on the basis of chromatographic mobilities and spectral characteristics.

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